A QCL-based Water Vapor Isotope Analyzer for Environmental Monitoring

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Outline

- Motivation and Background
- System Design
- Stability Performance and Detection Limit
- Field Deployment: Results and Lessons
- System Calibration
- Future Directions
Urban Water Cycle

“Fingerprint” water fluxes in the urban environment
Isotopes as Tracers

\[ \delta^{18}O = \left( \frac{\frac{^{18}O}{^{16}O}_{\text{sample}}}{\frac{^{18}O}{^{16}O}_{\text{std}}} \right) - 1 \]

- Standard = Vienna Standard Mean Ocean Water (VSMOW)
- Standard:
  \[ ^{18}O / ^{16}O = 2,005.20 \pm 0.43 \text{ ppm} \]
- Reported in ‰ ("per mil")

Sensor Applications and Requirements

Applications

• Provide transformative observational capabilities
  ➢ Environmental monitoring of urban watersheds
  ➢ Climatological assessments at regional and global scales
• Study coupled water, carbon, and nitrogen cycles in urban environments

Requirements

• Fast (1-10 Hz)
  ➢ To resolve turbulent fluxes
• Sensitive
  ➢ To resolve (1 ‰ @ 10Hz) isotopic ratio changes
• Robust and steady
  ➢ To be field-deployable
## Line Selection

**CW QCL**
\[ \lambda = 7.12 \, \mu m \]

- Similar lower vibrational energy states \( (\Delta E = 5.5484 \, \text{cm}^{-1}) \) for better immunity to temperature fluctuations \( (\Delta \delta = 0.1\% \text{ for } \Delta T = \pm 0.5 \, \text{C}) \)
- Comparable peak absorption for both target lines

### Table: Isotope Wavenumber and Intensity

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Line Intensity ((\text{cm}^{-1}/\text{molecule, cm}^{-2}))</th>
<th>Lower Vibrational Energy State (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{18})O</td>
<td>1389.91</td>
<td>1.08E-22</td>
<td>604.79</td>
</tr>
<tr>
<td>(^{16})O</td>
<td>1390.52</td>
<td>3.59E-22</td>
<td>610.34</td>
</tr>
</tbody>
</table>
System Design

- Attenuation of optical power
- 3.5 m multipass cell
- Cell housing windows at Brewster angle and allow for beamsplitting
- Etalon for frequency calibration
- Operation at reduced pressure (100 Torr)
  - Eliminate influence from adjacent lines
Retrieval Process

• Custom LabView software
  ➢ Real time acquisition and retrieval (@1 Hz)
• Model: line-by-line spectral modeling (Voigt Profile)
• Retrieved parameters
  ➢ Concentrations
  ➢ Isotopic ratio δ¹⁸O
  ➢ Additional Parameters
    ▪ Polynomial baseline
    ▪ Background water absorption fitting
System Performance: 
Stability & Detection Limits

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}_2^{16}\text{O}$</th>
<th>$\text{H}_2^{18}\text{O}$</th>
<th>$\delta^{18}\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s detection limit</td>
<td>2.2 ppm</td>
<td>7.0 ppb</td>
<td>0.25 ‰</td>
</tr>
<tr>
<td>Ultimate detection limit (at 160s)</td>
<td>0.6 ppm</td>
<td>1.7 ppb</td>
<td>0.04 ‰</td>
</tr>
</tbody>
</table>
Field Deployment, Beltsville, MD

~2.5 m off ground ~ 250 m footprint
Field Results and Lesson Learned

- Concentration is the only in-field comparison
- Delta measurement suffered from:
  - fringe noise caused by the detector
  - system temperature instability
Temperature stabilization

- Goals:
  - To avoid condensation
  - Stabilize sample gas temperature
  - Stabilize optical system
    - Using convective heating instead of conductive heating to minimize uneven temperature distribution of the system

- Thermal design:
  - Optical system thermally isolated by Styrofoam enclosure
  - Using heated sample line for gas inlet
  - Using Air-therm ATX heater to keep the system temperature at set-point

- Stability: within ±0.1 C at 40 C over 66 hours in lab condition
System Performance: Concentration Calibration

Li-Cor 610 Dew Point Generator

Calculated Dew Point Generator Concentration (ppm)

Measured Concentration (ppm)

Measured vapor concentration
Linear fit
\[ y = 0.91327x - 450.93554 \]
\[ R = 0.99996 \]
System Performance: $\delta^{18}O$ Calibration

- Calibration process;
- Calibration period $T$: system stability time $T$ at required detection limit

- Los Gatos nebulizer
- Known isotopic standards
Fringe noise from detector is limiting system accuracy.

Can be subtracted out by measuring zero gas repeatedly.

Further calibration underway.
Conclusions & Future Directions

• Precision: 0.25 ‰ for 1s and 0.04 ‰ for 160s for $\delta^{18}O$ measurement

• Lessons learned from field deployment: Temperature stabilization is critical

• Accuracy/calibration: challenges of water vapor isotope sensing: fringe noise

• Future field deployments
  – Broadmead, Princeton, NJ; Baltimore, MD
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